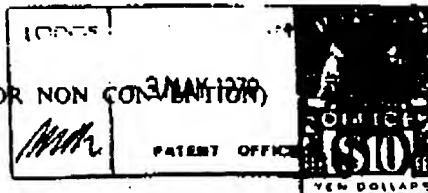


533791

AUSTRALIA
PATENTS ACT 1962

APPLICATION FOR A PATENT (CONVENTION OR NON CONVENTION)

57753/80



We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, a body corporate established under the Science and Industry Research Act 1949 and carrying on scientific and industrial research, of Limestone Avenue, Campbell, Australia Capital Territory, Commonwealth of Australia

COMPLETE AFTER PROVISIONAL SPECIFICATION No. 57753/80

hereby apply for the grant of a Patent for an invention entitled

"PURIFICATION OF BARK AND WOOD EXTRACTS FOR WOOD ADHESIVES"

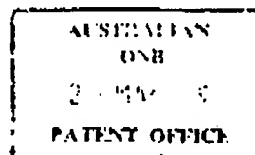
which is described in the accompanying ~~provisional~~ ^{complete} specification.

~~The application is a Convention application as it is based on the application(s) for patent or similar protection made~~

in
on
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on

under No.

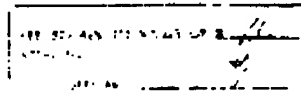
under No.



APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED

24-10-83



The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

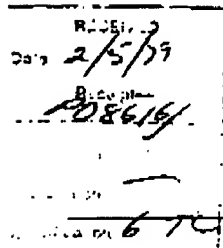
Dated this

1

day of

May

1979.



H. H. Rimington

(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant)

To: THE COMMISSIONER OF PATENTS
Davies & Collison, Melbourne and Canberra

COMMONWEALTH OF AUSTRALIATHE PATENTS ACT 1952-1973

577 53/80

DECLARATION IN SUPPORT OF AN APPLICATION
FOR A PATENT

In support of the Application No. 57753/80 made by Commonwealth Scientific and Industrial Research Organization (CSIRO) for a patent for an invention entitled "Purification of Bark and Wood Extracts".

I, DEREK BURGESS, of CSIRO, Limestone Avenue, Campbell, in the Australian Capital Territory, do solemnly and sincerely declare that I am authorised by CSIRO, the applicant for the patent, to make this declaration on its behalf.

YOSHIKAZU YAZAKI of 29 Hillston Road, Moorabbin; WILLIAM EDWIN HILLIS of 12 Lindsay Street, McKinnon and PETER JAMES COLLINS of 248 Myers Road, Bittern all in the State of Victoria.

is/are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:-

The actual inventor(s) is/are an officer(s) of CSIRO and the invention was made in the course of his/her/their official duties with CSIRO; the applicant is therefore entitled to apply by virtue of Section 54(1) of the Science and Industry Research Act 1949.

Declared at CANBERRA, this 11th day of July, 1980

R. Burgess

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(Original)

FOR OFFICE USE

53

577 53/80

Class

Int. Class

Application Number:
Lodged:Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the
amendments made under
Section 49.

and in correct for printing

LODGED AT SUB-OFFICE
23 APR 1980
MelbourneName of Applicant: COMMONWEALTH SCIENTIFIC AND INDUSTRIAL
RESEARCH ORGANIZATION

Address of Applicant:

Limestone Avenue,
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WILLIAM EDWIN HILLIS
PETER JAMES COLLINSAddress for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete specification for the invention entitled:

PURIFICATION OF BARK AND WOOD EXTRACTS
FOR WOOD ADHESIVESThe following statement is a full description of this invention,
including the best method of performing it known to us :-

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This invention relates to the preparation of bark and wood extracts which are suitable for use as wood adhesives.

5 The bark and wood extracts of a number of commercially important trees contain polyhydroxy phenols of which some are polyflavoroid in nature and can form condensation products with formaldehyde to thereby act as bases for wood adhesives. Such condensation products have been widely studied particularly with a view to
10 obtaining suitable adhesives for plywood and particle-board. The aforementioned bark and wood extracts are well known in the art and may be obtained, for example, by simple batch extraction of comminuted wood and bark with hot water at about 100°C. In some cases alkalis
15 such as sodium hydroxide or sodium sulphite may be added to promote extraction of the phenols or to suppress oxidation and degradation of the extract. However difficulties have been encountered primarily due to excessive viscosity of the extracts and the difficulty
20 in obtaining uniformity in product quality.

We have now found that upon fractionating aqueous extracts of wood and bark according to the molecular size (or weight) to find the most suitable and effective fraction of the extracts for condensation of the proantho-
25 cyanidin type compounds present with formaldehyde to form wood adhesives, that all fractions, except the lowest molecular size fraction containing monomers, dimers and oligomers and carbohydrates, have similar suitable condensation properties. This is shown in the
30 formation of similar and high amounts of formaldehyde precipitate (e.g. see Table 2 which follows). This suggested that removal of the highest molecular size fraction - the high viscosity producing fraction - would leave an easily handled material with suitable adhesive forming properties.

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It is therefore an object of the present invention to prepare purified and concentrated wood and bark extracts having a molecular size (or weight) which is most suitable for the preparation of wood adhesives.

5 According to the present invention there is provided a method for producing a low viscosity material from bark and wood suitable for use in a formaldehyde - condensation adhesive, which method comprises subjecting a conventional aqueous extract of bark or wood to ultrafiltration and
10 separating out that fraction which does not contain the high viscosity producing materials.

By low viscosity material we mean a material having an equivalent molecular weight of 10^6 or less.

By high viscosity producing materials we mean materials
15 which have an equivalent molecular weight of greater than 10^6 .

The term "equivalent molecular weight" as used herein, means the material has a molecular size equivalent to that of Dextran of the stated molecular weight.

Preferably, the fraction isolated lies within the
20 equivalent molecular weight range of 10^3 - 10^6 , thereby excluding the lowest molecular weight material, that is, material having an equivalent molecular weight of less than 10^3 , which contains a significant amount of formaldehyde-non-reactive material and water. However, the viscosity of
25 the fraction may be increased by removing the lowest molecular weight material since the molecular size distribution of the fraction shifts to that of the higher molecular size and also the purity of formaldehyde-reactive components increases.

30 We have found that increased yields of the desired material may be obtained by ultrafiltration with large quantities of water in the recirculating flow. It then becomes necessary, however, to remove a large quantity of water from the ultrafiltrate. It has been found that a
35 second ultrafiltration with membranes having nominal molecular weight limit (NMWL) characteristics of 10^3 removes this large quantity of water as well as those materials having an equivalent molecular weight of less than 10^3 , which tend to decrease the adhesive quality.

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To recover a large quantity of water from the second ultrafiltrate and to use the recovered water for extraction or ultrafiltration processes, the second ultrafiltrate, which contains ~~low molecular weight~~ ^(of equivalent MW < 10³) compounds of potential use, may be processed by reverse osmosis. ~~The low molecular weight~~ ^{These} compounds may be concentrated in the retentate and pure water obtained as the filtrate of reverse osmosis. This method is of importance for the fractionation of 60% aqueous acetone extracts, from for example *Pinus radiata* bark, and the recovery of the solvent.

The drying of polyphenol extracts on an industrial scale is carried out by spray-drying or vacuum evaporation in which the extracts may be changed by thermal degradation. Ultrafiltration and reverse osmosis avoid those deleterious effects associated with normal conventional dewatering processing. The process is athermal and permits removal of up to 90% of the water at ambient temperature, avoiding thermal and oxidative degradation of the product. The absence of phase change also results in lower energy costs.

The invention also extends to other extracts having an equivalent molecular weight of less than 10⁶, preferably an equivalent molecular weight in the range of 10³-10⁶, and the formaldehyde-condensation adhesives made from a mixture of such extracts with formaldehyde.

Preferred aspects of the invention will now be illustrated in more detail by reference to the following laboratory experiments.

Hot aqueous (100°C) extracts from *Pinus radiata* bark and a commercial wattle tannin were fractionated according to molecular weight by laboratory scale ultrafiltration. Spray-dried hot water extracts (2.0 g) were dissolved in water (50 ml) and 10% NaOH aqueous solution (0.6 ml) was added to adjust to pH 8.0. The solution was put into a Millipore 47 mm stirred cell and a Amicon Model 52 stirred cell with various ultrafiltration membranes and filtrations were carried under 0.35-1.40 kg/cm² nitrogen pressure at room temperature for 5-76.5 hours. The ultrafiltration

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membranes used were Pellicon PSVP (nominal molecular weight limit (NMWL); 10^6), PTHR (NMWL; 10^5), PTGC (NMWL; 10^4) and PSAC (NMWL; 10^3).

Fractionation results of the hot water extracts from *Pinus radiata* bark and the commercial wattle tannin by ultrafiltration are shown in Table 1:

TABLE 1

Molecular size distribution of the hot water extracts of *Pinus radiata* bark and of the wattle tannin

Fractions	Percentage of	
	100°C aqueous extracts of <i>P. radiata</i> bark	Wattle Tannin
More than 10^6 *	22.4	16.5
$10^5 - 10^6$	5.5	3.9
$10^4 - 10^5$	29.2	23.6
$10^3 - 10^4$	11.5	6.6
Less than 10^3	31.4	49.4

*Containing compounds which have a molecular size equivalent to that of the corresponding number molecular weight Dextran.

Ultrafiltration of the extracts with PSVP membrane yielded 77.6% of the filtrate with a molecular size less than that of a 10^6 molecular weight Dextran. It also reduced the viscosity of the filtrate down to a level which is well below the upper viscosity limit permissible for the formulation of wood adhesives. The retentate was identified as the main viscosity control factor which causes excessive viscosity of the extracts.

Should it be necessary to control the rate of penetration of the purified extracts into wood, when used as a basis for adhesives this could be done, for example, by the addition of specified amounts of a gel-forming

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material of precisely known properties, or by the addition of suitable filler.

TABLE 2

Stiasny reaction precipitates of catechin and the various fractions of the 100°C aqueous extracts of *P. radiata* bark

Formaldehyde precipitate (%)	
Catechin	97.5
100°C aqueous extracts	81.0
Retentate $>10^6$ *	90.0
Ultrafiltrate $<10^6$	71.0
Fraction (10^5 - 10^6)	90.5
- (10^4 - 10^5)	91.5
- (10^3 - 10^4)	82.4
- ($<10^3$)	40.5

*Containing compounds which have a molecular size of the corresponding number molecular weight Dextran.

Analyses of compounds in each fraction revealed that the smallest molecular size (or weight) fraction contained all the monomers, dimers (procyanidins) and oligomers but compounds in the other fractions are basically of the same procyanidin type compound and the only difference is the degree of polymerization of the procyanidin unit among the fractions.

The amount of formaldehyde precipitate (Table 2) provides a reliable estimate of the total polyphenols which react with formaldehyde in adhesive formation.

The highest yield (97.5%) of the formaldehyde precipitate was obtained with 100% pure catechin which was used as a control for this experiment. The original 100°C aqueous extracts from *Pinus radiata* bark gave 81.0% yield of the formaldehyde precipitate. However,

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the retentate ($>10^6$) remaining after ultrafiltration with PSVP membrane gave a high yield (90%) of the precipitate. Chemical analyses revealed that the retentate consists of 95% procyanidin polymers and of 5% carbohydrates. Purity of procyanidin polymers in the fractions containing compounds with a molecular weight between 10^5 and 10^6 and also between 10^4 and 10^5 was even higher than that of the retentate ($>10^6$). A smaller molecular weight fraction (10^3 - 10^4) yielded 82.4% the formaldehyde precipitate indicating increasing amounts of non-reactive material. However, the purity of procyanidin polymers in this fraction was yet higher than that of the original 100°C aqueous extracts which contain the high viscosity producing material. The lowest molecular weight fraction gave 40.5% yield of formaldehyde precipitate. Analyses of this fraction ($<10^3$) revealed that it contained non-reactive polyphenols such as stilbenes and flavonols as well as 47% carbohydrates in which glucose and arabinose were the predominate sugars.

An embodiment of the present invention will now be described with reference to the accompanying drawing which schematically illustrates the fractionation of a hot water extract by ultrafiltration and reverse osmosis.

The aqueous extract (I) flows into the tank 1 after pH adjustment and is pumped into the ultrafiltration module 2. The liquid passes at high speed over the surface of the membranes of NMWL = 10^6 , components with equivalent MW $< 10^6$ and water pass through the membranes and the permeate (II) is collected in tank 3. The retentate is recycled and eventually concentrated as the highest molecular weight fraction (I'). The filtrate in the tank 3 is further filtered with a membrane of NMWL = 10^3 by ultrafiltration module 4 and recycled to concentrate a defined molecular weight component (molecular weight between 10^3 - 10^6). The

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- permeate (III) which was collected in the tank 5 and contained lower molecular weight components and water, is subjected to reverse osmosis with a membrane of NMWL-350 at high pressure in module 6. The low molecular weight components are concentrated to give product (III') and water is obtained as permeate from the reverse osmosis. The product (I') consists of high polymeric components with 95% procyanidin polymers and is the fraction producing high viscosity. The components may be useful as filler for wood adhesives. The product (II') is the most suitable fraction for wood adhesives. The fraction contains compounds with a certain molecular size (or weight) range and can be concentrated up to the suitable concentration for the formulation of wood adhesives.
- The product (III') consists of lower molecular size (or weight) components such as carbohydrates (glucose and arabinose as predominant sugars in the case of *Pinus radiata* bark extracts), monomeric flavonoids and stilbenes.
- The purified extracts may be substituted for phenols and other tannins in adhesive formulations, for example in a typical wattle tannin adhesive comprising

	<u>Parts by weight</u>
Wattle tannin	100
Water	113
Sodium hydroxide	0.9
Wood flour	10-12.5
Paraformaldehyde	8

- When extracts purified in accordance with the above described procedure were substituted for wattle tannin in such an adhesive formulation, laboratory adhesion tests revealed that strong bonds could be obtained with adhesives formulated with different molecular weight fractions of the hot water extracts from *Pinus radiata* bark (Table 3).

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TABLE 3

Bond strength of plywood glued with adhesives
from the fractions of *Pinus radiata* bark extracts¹⁾

	Failing load (MPa) and wood failure (%)					
	Dry		24 h Cold soak		72 h Boil	
Fraction ($<10^6$) *	4.253	89	3.659	21	3.323	80
Fraction (10^3 - 10^6)	4.090	98	4.206	95	2.912	90

1) Adhesion tests were carried out according to
AS1321.3-1976 using two-ply tensile shear test specimens.

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*Veneer species; Coachwood (*Ceratopetalum apetalum*),
Tulip Oak (*Argyrodendron* sp.), veneer moisture
content; 5%, 12%, assembly time; 2 hour, 2 hour for
fractions ($<10^6$ molecular size) and ($10^3 - 10^6$),
respectively.

The nominal molecular weight limits (NMWL) of the
membranes used here are applicable only for the
fractionation of *Pinus radiata* bark extracts and
particularly PSVP membrane with NMWL 10^6 was used only
as a suitable membrane for removing high polymeric
materials at this moment. Consequently, it is necessary
to select the most suitable membranes according to the
purpose of the process in order to fractionate and
purify the extracts from other barks or woods.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for producing a low viscosity material from bark or wood suitable for use in a formaldehyde-condensation adhesive, which method comprises subjecting a conventional aqueous extract of bark or wood to ultrafiltration and separating out that fraction which does not contain the high viscosity producing materials.
2. A method as claimed in claim 1 and including the additional step of subjecting the separated fraction to a second ultrafiltration in order to remove those materials having an equivalent molecular weight of less than 10^3 .
3. A method as claimed in claim 2 and wherein the permeate is subjected to reverse osmosis in order to separate those materials having an equivalent molecular weight of less than 10^3 from the water.
4. A method as claimed in any one of the preceding claims wherein a membrane with NMWL of 10^6 is used in the only or first ultrafiltration step.
5. A method as claimed in claim 2 or 3. or claim 4 when appended to claim 2 or claim 3, wherein a membrane with NMWL of 10^3 is used for the second ultrafiltration step.
6. A method as claimed in any one of claims 3, or 4 or 5 when dependent on claim 3, wherein a membrane with NMWL of 350 is used for the reverse osmosis.
7. A method as claimed in any one of the preceding claims, wherein an extract of pinus radiata bark is used.

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8. A method as claimed in claim 7 wherein the extract is a hot aqueous extract which has been adjusted to a pH of 8 with an hydroxide.
9. A low viscosity material suitable for use in a formaldehyde-condensation adhesive whenever produced by a method defined in any one of the preceding claims.
10. A formaldehyde-condensation adhesive with uniform quality when made from a material as defined in claim 9.
11. A method as claimed in claim 1 of producing a low viscosity material from bark or wood suitable for use in a formaldehyde-condensation adhesive substantially as herein described with reference to the laboratory experimental data or accompanying drawing..
12. A formaldehyde-condensation adhesive as claimed in claim 10 substantially as herein described with reference to the laboratory experimental data or accompanying data.

DATED this 14th day of October, 1983
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH
ORGANIZATION
by its Patent Attorneys
DAVIES & COLLISON.

